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Crystal structure of sparteinium tetrachlorocuprate monohydrate-packing polymorph

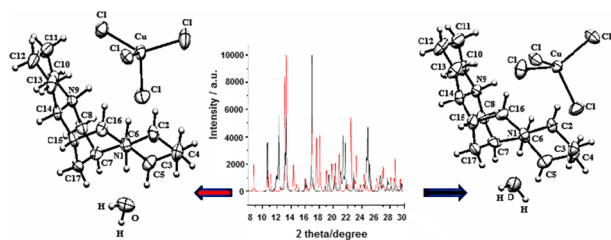
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Abstract

A new polymorph of sparteinium tetrachlorocuprate monohydrate $[(C_{15}H_{28}N_2)CuCl_4 \cdot H_2O]$ is reported. The structure of the analyzed crystal was solved in the orthorhombic $P2_12_12_1$ space group with the following unit cell parameters at 295 K: $a = 9.7722(2)$ Å; $b = 13.4582(3)$ Å; $c = 15.1582(3)$ Å. The various types of hydrogen bonding interactions existing in the crystal structure of this salt were compared with the data of the previously reported polymorph. XRPD measurement proved that our salt consists of a pure phase of the new polymorph. Cooling down the salt to ca. 230 K caused its color to change from orange-brown to yellow. DSC experiments revealed that during the cooling an endothermic process takes place corresponding to the mentioned color change of the salt.

Graphical abstract



Keywords IR spectra · DSC · Hydrogen bonding · Polymorphism · Raman spectra

Introduction

(–)-Sparteine, an alkaloid naturally occurring in plants from *Lupinus*, *Laburnum*, *Spartium*, *Genista*, *Saratamnus* and other genera of Fabaceae family is a sodium channel inhibitor used as an antiarrhythmic drug. Sparteine occurs

in nature as levo- and dextrorotatory. The latter enantiomer, called pachycarpine, is toxic.

The presence of two amine atoms in the structure of sparteine led to its use as a bidentate ligand in various complexes (e.g., involving copper [1–13]). Following quaternization of both nitrogen atoms in the molecule sparteine was used as a dication in metalloorganic copper salts [14, 15].

While searching for novel complexes with thermochromic properties we synthesized a previously described salt of this alkaloid with copper ions (Fig. 1). The synthesis was performed according to the reported methods so we expected a salt identical with that obtained before [14, 15].

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s00706-019-02426-2>) contains supplementary material, which is available to authorized users.

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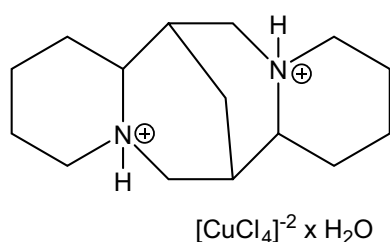


Fig. 1 Structure of sparteinium tetrachlorocuprate monohydrate salt

Table 1 Selected geometrical data for salt **1** obtained at room temperature

	1		1
Cu–Cl1/Å	2.371	Cl1–Cu–Cl2/°	102.29
Cu–Cl2/Å	2.215	Cl1–Cu–Cl3/°	100.51
Cu–Cl3/Å	2.211	Cl1–Cu–Cl4/°	117.64
Cu–Cl4/Å	2.214	Cl2–Cu–Cl3/°	133.87
		Cl2–Cu–Cl4/°	100.28
		Cl3–Cu–Cl4/°	103.73
N1–N9/Å	3.667	Cu–O/Å	7.939
Cu–N1/Å	5.350	N1–O/Å	2.733
Cu–N9/Å	4.471		

Results and discussion

Selected interatomic bond lengths and angles for sparteinium tetrachlorocuprate monohydrate (**1**) salt obtained at room temperatures are shown in Table 1. Summary of crystallographic data for salt **1** are shown in Table 2.

Crystallographic properties of the obtained salt

The salt obtained by us, identical with those reported by Lee et al. [14] and Jasiewicz et al. [15], markedly differed from them in parameters of the unit cell and its volume, with isomorphic space group ($P2_12_12_1$) and same number of molecules in unit cell ($Z=4$). The salts described in this paper and in [14] were obtained using similar methods and same solvent (ethanol) and copper salt ($\text{CuCl}_2 \times 2\text{H}_2\text{O}$), however, sparteine used by us was in the form of sulfate whereas that used in [14] was pure alkaloid. The salt described in [15] has been obtained as a byproduct during the synthesis of α -isosparteine tetrachlorocuprate. Comparison of the crystallographic data presented in [14, 15] shows that in both papers this same polymorph is described. Crystallographic studies were performed at similar room temperatures. This is significant, because this salt exhibits thermochromic properties at low temperatures. Crystallographic examination of our salt was also carried out at 100 K, because this salt at

about 230 K starts slowly changing the color from orange to yellow which should reflect changes in crystallographic structure.

XRPD measurements of the batch procured in our experiments show that the new polymorph formed as a pure phase (Fig. 2). Figure 3 shows the comparison of XRPD patterns for salt **1** (red line) and salt reported in [15] (black line) calculated from single-crystal data of both polymorphs.

The molecular units of salt **1** at both measured temperatures are built through the formation of several weak hydrogen bonds between the sparteinium nitrogen atoms, chlorine atoms of the anions, and water molecules. The N...Cl distances in reported polymorph are only slightly shorter (3.183 Å) than those reported in [14] (3.280 Å) and [15] (3.286 Å). These bonds are shorter in 100 K (3.143 Å). The H...Cl distances range from 2.220 to 2.367 Å (shorter than sum of Van der Waals radii = 2.95 Å) with the N–H...Cl angles are between 152.94° and 166.76° (Figs. 4, 5).

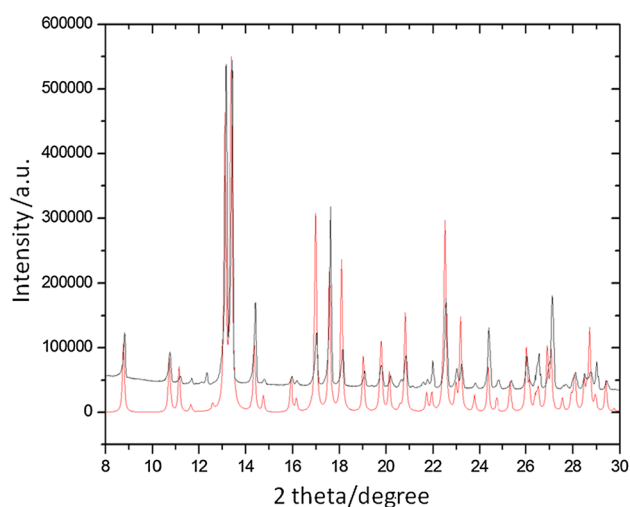
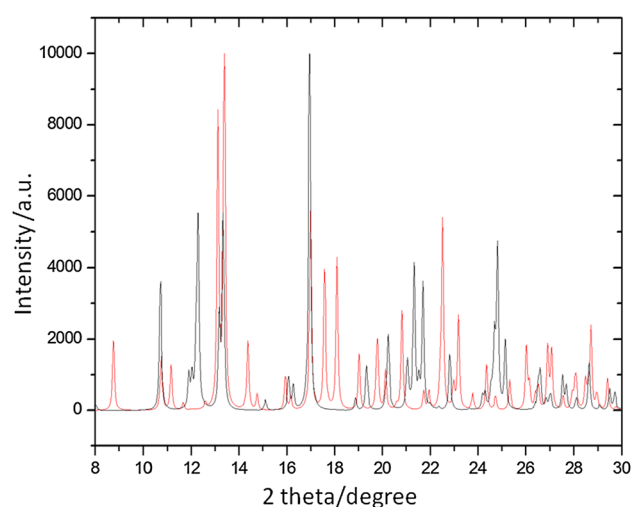
The shortest distance between chlorine atoms of two different CuCl_4^{2-} ions in salt **1** is 3.896 Å (at 295 K) and 3.820 Å (at 100 K), not particularly greater than the sum of van der Waals radii for two chlorine atoms (3.60 Å) and considerably shorter than the values reported in [14] (4.523 Å) and [15] (4.525 Å). The near distance between copper atoms in salt **1** (7.897 Å) is shorter compared to those in the polymorph described earlier where these distances are 8.221 Å [14] and 8.228 Å [15], respectively. Distances between copper atoms and nearest chlorine atoms not linked to the former are 5.757 Å for salt **1** (5.950 Å and 5.951 Å for previously described polymorph in [14, 15], respectively). This distance is too long to allow formation of Cu–Cl–Cu bridge.

The most obvious difference between the two polymorphs is the orientation of the CuCl_4^{2-} anions relative to sparteinium molecules (and also H_2O molecules). The average O–H...Cl distances lie within 2.320–2.530 Å range for one chlorine atom and within 2.279–2.903 Å range for the other chlorine atom. These values pertain to the same anion in case of the reported salt, and to two different anions for salts reported in [14, 15], which is shown in Fig. 1S (supplementary materials).

While cooling down a sample of the salt in liquid nitrogen, we noticed that it changes the color from orange to yellow and returns quickly to the former color following slight warming (Photo 1—supplementary materials). This process was repeated several times without any visible change in the external appearance of the sample (crystals did not change their shape or color). We decided to perform crystallographic measurements of a monocrystal at 100 K. Much to our surprise, while changing color, the crystal did not alter drastically the parameters of the unit cell. When analyzing particular fragments of the salt and comparing results to the previously obtained structure at 295 K we concluded that the differences in values of relevant distances in

Table 2 Crystal data, data collection, and structure refinement for salt **1** at 295 K and 100 K, respectively

Chemical formula	$C_{15}H_{30}N_2O_1Cu_1Cl_4$	$C_{15}H_{30}N_2O_1Cu_1Cl_4$
M_r	459.75	459.75
T/K	295	100
Wavelength/ \AA	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions		
$a/\text{\AA}$	9.7722(2)	9.7152(1)
$b/\text{\AA}$	13.4582(3)	13.3623(2)
$c/\text{\AA}$	15.1582(3)	15.0337(2)
$V/\text{\AA}^3$	1993.55(7)	1951.64(4)
$D_{\text{calc}}/\text{Mg m}^{-3}$	1.532	1.565
Z	4	4
Absorption coefficient/ mm^{-1}	1.636	1.671
$F(000)$	956	956
Crystal size	$0.13 \times 0.04 \times 0.03$	$0.13 \times 0.04 \times 0.03$
Theta range for data collection/ $^\circ$	2.905–26.368	2.925–26.357
Index ranges	$-11 \leq h \leq 12$ $-16 \leq k \leq 16$ $-18 \leq l \leq 18$	$-12 \leq h \leq 11$ $-16 \leq k \leq 16$ $-18 \leq l \leq 18$
Reflections collected	16,079	15,759
Independent reflections	4069 [$R_{\text{int}}=0.0299$]	3979 [$R_{\text{int}}=0.0180$]
Data/restraints/parameters	4069/0/208	3979/0/208
Goodness-of-fit on F^2	1.056	1.061
Final R indices [$I > 2\sigma(I)$]	$R1=0.0265$ $wR2=0.0654$	$R1=0.0152$ $wR2=0.0403$
R indices (all data)	$R1=0.0295$ $wR2=0.0680$	$R1=0.0156$ $wR2=0.0406$
Largest diff. peak and hole/ $e \text{\AA}^{-3}$	0.446 and -0.414	0.254 and -0.326

**Fig. 2** XRPD patterns of the material obtained from our synthesis (black line) and XRPD patterns for salt **1** calculated from single-crystal data measured at 295 K (red line) (color figure online)**Fig. 3** Comparison of XRPD patterns for salt **1** (red line) and salt reported in [15] (black line) calculated using single crystal data from both polymorphs (color figure online)

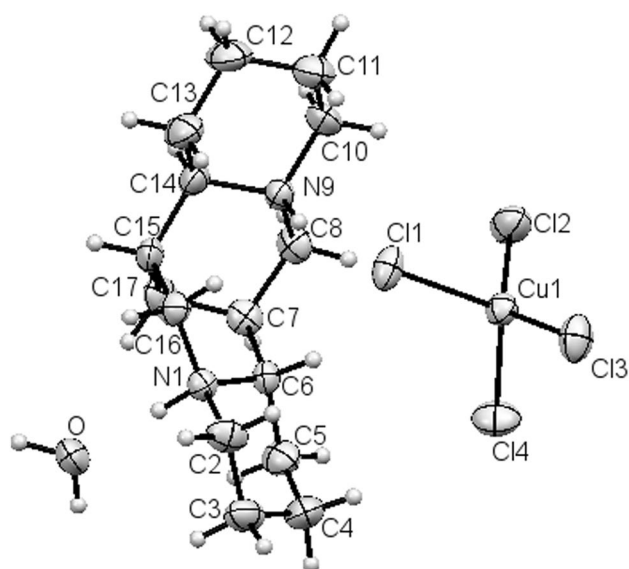


Fig. 4 Molecule of salt **1** in the crystal. Ellipsoids correspond to 50% probability levels

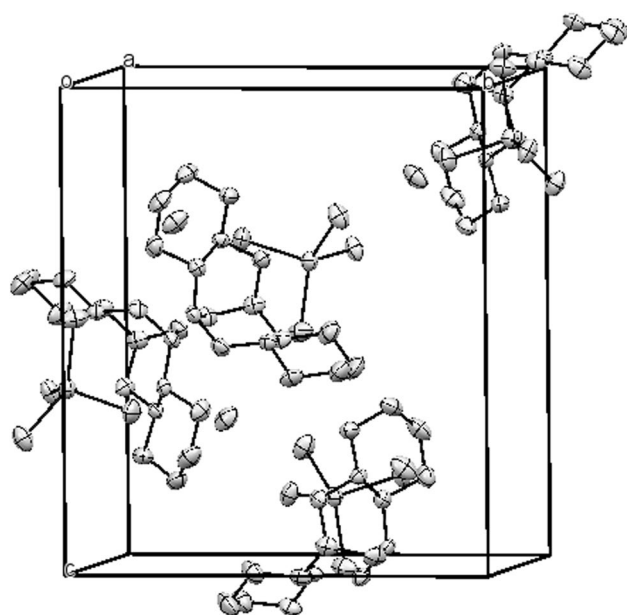


Fig. 5 A view of crystal packing of salt **1** in projection along the *a* axis

both temperatures are almost identical. Distance differences between copper ions were within the 0.05–0.17 Å range, whereas those for chlorine atoms spanned the 0.076–0.102 Å range. Likewise, angles occurring in the CuCl_4^{2-} tetrahedral ion are almost identical.

Looking at the arrangement of CuCl_4^{2-} ions in the unit cell along the *z* axis one can observe that they are located in planes parallel to (010). When analyzing mutual shift

of these planes one notices that they are closer together at 100 K (6.680 Å) than at 295 K (6.775 Å). Likewise, distances between adjacent anions are shorter at 100 K (9.715 Å) than at 295 K (9.794 Å).

Considering how vastly different parameters of the unit cell of the obtained salt are, compared to the one obtained earlier by Korean researchers [14], we decided to obtain the salt by proceeding in manner identical to the one reported by them. Pure base (sparteine) was obtained from its sulfate by neutralization. The achieved sparteine exhibited properties agreeing with literature data [14]. Crystallographic studies were performed on the obtained crystals of the salt and it turned out that crystal parameters were identical with those of crystals acquired earlier by us. Despite repeated efforts, we did not manage to obtain crystals of the salt with cell parameters reported in [14].

TGA and DSC studies of the salt

TGA plot (Fig. 6) reveals loss of crystal water started at 80 °C, and completed at ca. 100 °C. Between 100 and 280 °C two molecules of HCl were removed (mass loss ca. 15.9%), and finally between 280 and 500 °C sparteine was removed from the sample (mass loss ca. 51%). The remnant is CuCl_2 (29.2% of the initial mass).

As mentioned earlier, when cooled down the compound starts changing its color from orange-brown to intense yellow. The process spans several dozen degrees and is reversible, i.e., the initial color returns upon slow warm-up. The results of low-temperature DSC performed in the +7 °C to –140 °C range (282–135 K) are shown in Fig. 2S (supplementary materials). During the cycle starting with cooling, an endothermic process takes place (0 °C to ca. –120 °C) with a maximum recorded at –35.76 °C and reflected as a wide broad peak corresponding to the previously described color change of the salt. Further heating of the sample leads to the appearance of exothermic, very broad peak (at –125 °C to –30 °C) with a maximum at –99.71 °C. Later cycles of cooling and heating lead to the disappearance of the effect. Subsequently, the examined sample was kept tightly closed and measurements were repeated after 2 and 4 weeks. A similar DSC plot was obtained. Based on these observations and previous literature reports [14], we can conclude that, transitions from one organizational state to another are possible but require both adequate timing and conditions.

IR spectra and Raman spectra of the salt at room temperature

All IR and Raman vibrations are listed in supplementary materials. The infrared spectrum of salt **1** is mainly

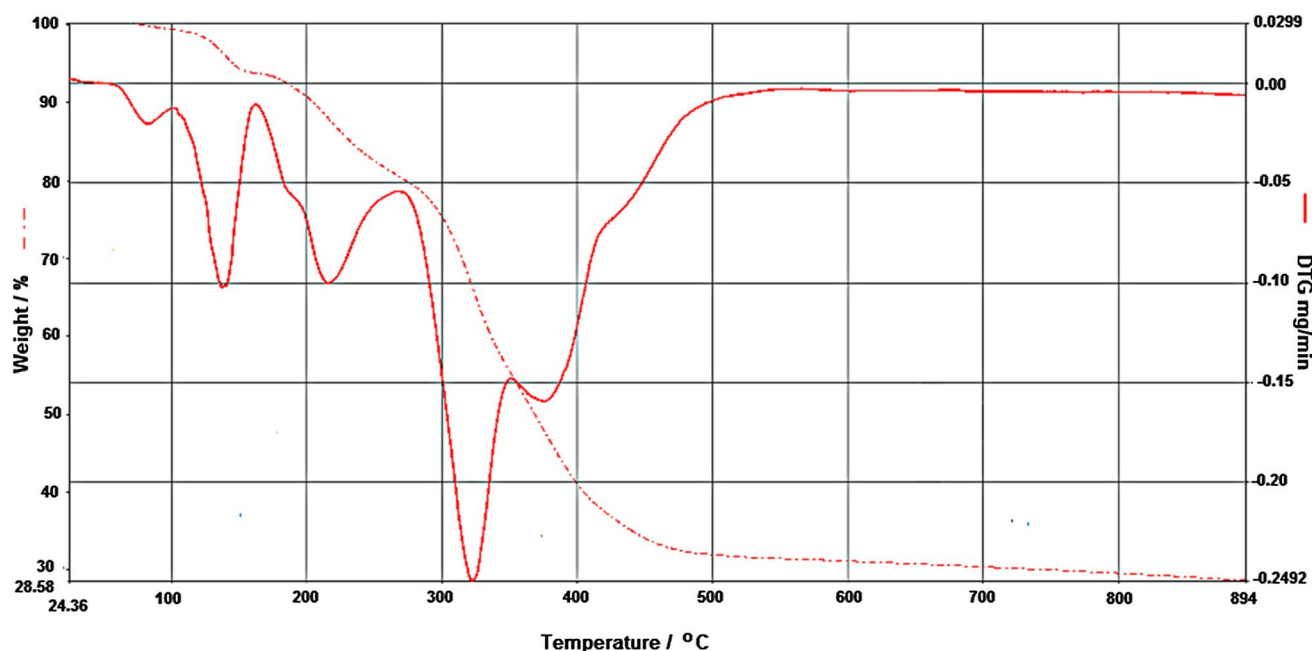


Fig. 6 TGA plot of salt 1

characterized by the vibrational modes of NH, OH and Cu–Cl units (groups). The Raman spectrum of **1** is mainly characterized by the vibrational modes of Cu–Cl fragments of CuCl_4^{2-} ions.

Vibration characteristic for two fragments of the salt (CuCl_4^{2-} ion and sparteine ligand) can be discerned in both modes. The IR spectrum of salt **1** shows very broad band at 3436 cm^{-1} attributed to $\nu(\text{NH})$ or $\nu(\text{OH})$, while the Raman spectrum shows no bands in this region. The CuCl_4^{2-} room-temperature IR spectrum shows two strong well-resolved bands near 293 cm^{-1} and 184 cm^{-1} attributed to A_1 stretching frequency and the T_2 frequency, respectively. In Raman spectrum one could notice a $\nu(\text{Cu–Cl})$ symmetric stretching frequency at 282 cm^{-1} and a T_2 frequency at 181 cm^{-1} . These values are comparable to the literature data for CuCl_4^{2-} salts [16, 17].

Conclusion

Differences in crystal structures occurring between the examined salts with identical molecular formulas permit to conclude the presence of polymorphic variants of the same salt. The study indicates that the reported variant is a stable structure. We did not observe any major structural alterations in this salt at room temperature or at 100 K. Most likely, alterations in crystal structures may occur at temperatures higher than room temperature. Unfortunately, crystals obtained in here were destroyed even with slight heating under a nitrogen sweep. This effect can probably be linked

to removal of water molecules from crystals during heating. We were not able to obtain polymorph described in [14, 15], and therefore, comparison of spectroscopic data for various polymorphs is not possible except for pointing out the differences in crystallographic structure. DSC-generated data show that changes taking place in crystals of the investigated species depend on the dynamics of heating/cooling manipulations. These changes vanish after several cycles of heating/cooling but reappear when examined samples are left alone for ca. 1 week or more.

Experimental

Infrared (IR) spectra were recorded with Nicolet iS50 FT-IR Spectrometer (Thermo Scientific, Warsaw, Poland), using ATR technique. Raman measurements were performed using a Thermo Scientific™ DXR™ 2xi Raman imaging microscope equipped with a 780 nm laser (Thermo Scientific).

Differential scanning calorimetry (DSC) was performed with a DSC Pyris 1 (Perkin Elmer) using aluminum sample pans. The DSC experiments were carried out in a nitrogen atmosphere with a temperature range from 7 to $-140\text{ }^\circ\text{C}$; scanning rate $10\text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analysis (TGA) was performed with a TGA Pyris 1 (Perkin Elmer) in a nitrogen atmosphere in $25\text{--}900\text{ }^\circ\text{C}$ temperature range (scanning rate $10\text{ }^\circ\text{C min}^{-1}$).

Single-crystal X-ray experiments were performed at 100 K or 295 K. The data were collected using a Supernova kappa diffractometer with Atlas CCD detector (Agilent

Technologies). Collected data were integrated with CrysAlis Pro software [18]. The structures were solved using direct methods with the SHELXS-2013 software and the solutions were refined using SHELXL-2014/6 program [19]. CCDC-1865419 and 1865420 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via: www.ccdc.cam.ac.uk/data_request/cif. X-ray powder diffraction was performed with PAN analytical Empyrean powder diffractometer equipped with PIXcell^{3D} detector and a Cu-K α radiation source.

Sparteinium tetrachlorocuprate monohydrate (**1**) was obtained using two methods:

A. from sparteinium sulfate equimolar amounts of ethanolic solutions of sparteine sulfate and hydrated copper(II) chloride were mixed, and yellow precipitate was formed. Concentrated HCl was added to dissolve the precipitate, upon which the solution turned green. Solvent evaporation led to an appearance of an orange-colored substance. Ethanol and conc. HCl were then added and the mixture was heated to boiling. A yellow-colored liquid formed from the abovementioned orange precipitate was transferred to another beaker and cooled down. Crystallization yielded small yellow-colored needles which were subsequently used in crystallographic studies.

B. from sparteine sparteine was obtained from sparteine sulfate by alkalyzing solution of this salt. Sparteine was then dissolved in saturated methanolic HCl solution. The latter was then mixed with copper(II) chloride solution and the whole was slightly heated. The obtained solution was left to start crystallization. This led to a product in the form of orange crystals a few of which were chosen for crystallographic studies.

The process of color change and its extent for a given salt was concluded via cooling of the sample (ca. 10 mg) placed in an NMR tube with internal thermocouple positioned in the cooling mixture (solid CO₂/acetone or liquid nitrogen).

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